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Textural properties and carbon dioxide adsorption enhancement of Mordenite zeolite synthesized in the presence of a new organic template

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Abstract. Recently, a great attention has been given to the adsorption and separation of CO_2. Carbon dioxide is the main greenhouse gas, which causes a severe global warming. Industrially, the most used adsorbents are metal–organic frameworks, activated carbons, silica and alumina. In the last recent years, zeolites have been found suitable materials for this polluting gas elimination. Their structure, high surface area and physic-chemical properties such as hydrothermal and mechanical resistant made of them good adsorbents. In this work, Na-mordenite zeolite synthesis with remarkable mesoporosity was successfully synthesized by soft templating method in the presence of *N*,*N*-dimethylaniline as novel organic template and characterized with several techniques (XRD, SEM and BET). The prepared material was tested in environment protection. In the first it was ion exchanged by two alkali metal cations (K^+, Cs^+). Intracrystalline diffusion and alkalinity of zeolites were attributed high adsorption capacities of CO_2. Carbon dioxide capturing capacity increased in the sequence Cs-MOR>K-MOR>Na-MOR.

Keywords: Meoporous mordenite, Soft templating, Alkali cations, CO_2 adsorption.

Textural properties and carbon dioxide adsorption enhancement of Mordenite zeolite synthesized in the presence of a new organic template

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Abstract. Mesoporous Na-mordenite zeolite was successfully synthesized by soft templating method and in the presence of *N,N*-dimethylaniline as a new organic template. It was then characterized with several techniques (XRD, SEM and BET). The prepared material was then ion exchanged by two alkali metal cations (K^+, Cs^+). The high intracrystalline diffusion and alkalinity of zeolites were attributed on adsorption capacities of CO_2. Carbon dioxide capturing capacity increased in the sequence Cs-MOR>K-MOR>Na-MOR.

Keywords: Meoporous mordenite, Soft templating, Alkali cations, CO_2 adsorption.

1 Introduction

Zeolites are crystalline aluminosilicates with well-defined microporous structure [1]. Their frameworks are formed by TO_4 tetrahedra, where T = Si and Al, generating three-dimensional structures defined by channels pores and cavities, which can be used as adsorbents [2], catalysts [3], and ion exchangers [4] in industry. They are classified according to the number of opening pore, 8 MR (Member of Rings) as small-pore, 10 MR as medium-pore, 12 MR as large-pore, and extra-large pore more than 12 MR systems [5]. As one of the most important zeolites is mordenite from structural type MOR. It is high-silica large pore zeolite with a channel system composed of a straight 12 member rings (0.65 x 0.7 nm), which are connected by small side-pockets with 8 member rings pores (0.26 x 0.57 nm) parallel to the *c*- axis, and an additional 8 member rings channel (0.34 nm x 0.48 nm) parallel to the *b*- axis [6]. The mordenite chemical composition is: $Na_8Al_8Si_{40}O_{96}nH_2O$ [7]. The unit cell parameters of sodium mordenite are: a = 18.121 Å, b = 20.517 Å, and c = 7.544 Å [7]. The first claim to the synthesis of mordenite was by Leonard in 1927, and the first substantiated synthesis was made by Barrer in 1948 [8]. Like most zeolites, mordenite is widely used in adsorption and heterogeneous catalysis [9].

The technological exploitation of zeolites materials, notably in selective adsorption of hazardous molecules is based on the similarity between size and polarity of the molecules and pore dimensions [10], which leads to slow diffusion and hence the possibility of significant reductions in their performance. Some processes involving molecules larger than the zeolite pore apertures that accumulate into the zeolite canals and decrease the zeolite lifetime [11–13]. Among the various strategies for overcoming such diffusion-related limitations in performance, the generation of mesopores within the microporous bulk phase has attracted particular attention [14].

Introducing mesoporosity in zeolites is a long-standing goal in this mature field. Much effort in zeolites synthesis has been devoted to creating extra-large pore zeolites, with some producing beautiful, open structures. Different strategies have been productive in extending the range of zeolite micropore sizes. The field of hierarchical zeolites is emerging as a simple and effective alternative that overcomes the pore size limitation of zeolites by creating materials with a combination of both zeolitic microporosity and additional larger mesoporosity. In these cases, different processes have been done, such as zeolite demetallation or recrystallization around a surfactant, hard templating and downsizing the zeolite particle size which are helpful for improving intracrystalline diffusion and enhancing the zeolite lifetime [15,16].

On the other hand, carbon dioxide is greenhouse gas which causes a major environmental problem, and many efforts have been made to reduce its emission. The increase in atmospheric carbon dioxide has been a primary contributor to global warming over the past century. Different processes can be used for CO_2 capture and separation such as absorption, cryogenic and membrane separation, and micro-algal bio fixation [17]. But they are limited by high cost of operation, production of unwanted by-products, or cumbersome operation [18]. Among several processes that have been proposed; the adsorption that has gradually become an economically attractive alternative due to its low energy cost, stable performance and easy operation [19,20]. A large number of adsorbents have been investigated such as metal organic frameworks (MOFs) [21], mesoporous silica [22], activated carbon [23], polymers [24] and zeolites [25]. Because of their affinity to polar molecules and facile modification, zeolites are the most preferred adsorbents for CO_2. One of the most zeolites that have widely used in CO_2 adsorption is mordenite. The adsorption process over this zeolite was always limited by its chemical composition and its pore size [26,27].

In this study, two new ideas were investigated. Direct hydrothermal synthesis and characterization of mesoporous mordenite using soft templating method as a new strategy for creating expanded pores to improve intracrystalline diffusion. Then, the obtained material was chemically treated with different alkali metal cations (Cesium and Potassium) by ion exchange operation to have basic varieties of zeolites able to capture CO_2 as acid gas [28].

2 Experimental

2.1 Materials

The reagents used were: *N*,*N*-dimethylaniline (Sigma-aldrich, 99 %) as organic template, porous silica gel powder (Fluka) as silicium source, sodium hydroxide pellets (Sigma-aldrich, 99.998 %) as mineralizator agent, aluminum chloride hexahydrate (Sigma-Aldrich, 99 %) as aluminum source, cesium chloride (Sigma-aldrich, 99.9 %) and potassium chloride (Sigma-aldrich, 99 %) were used for ion exchange operation, and demineralized water purified using Water Purification System Milli-Q (MERCK).

2.2 Characterization

The pH value of the homogenous hydrogel was measured by inoLab pH 730 (WTW). The porosity occupied by the organic template was released by a calciner (Nabertherm). The crystalline structure was determined by X-ray diffraction (Bruker AXS D8 ADVANCE diffractmeter with a CuKα radiation source). Thermal analysis (TG/dTA) experiments were carried out by a TA Micrometrics 2050 TGA apparatus. Porosity of the material was measured by nitrogen physisorption (Micromeritics ASAP 2020). The FTIR spectra were taken in KBr pellets using Alpha-Bruker FTIR spectrophotometer. The morphology of the material was inspected by SEM (JEOL JSM 6610 LA).

2.3 Mordenite synthesis

The hydrogel mixture was prepared by the following manner: 3 g of silica gel powder mixed with 1 g of sodium hydroxide solution, then 2.7g *N*,*N*-dimethylaniline was added drop wise under stirring in a known volume of demineralized water. One hour later, 0.654 g of aluminum chloride was added to the first mixture. This new mixture was stirred for 24 h in room temperature till formation of homogenous hydrogel. After stirring, pH value was taken (pH = 12.81) and the hydrogel was allowed to aging. One hour later, the homogeneous mixture was transferred to a Teflon lined autoclave with a volume full capacity of 50 ml and carried out in crystallization temperature of 423 K under autogenous pressure, for 6 days. After crystallization had been completed the autoclave was rapidly cooled and the recovered white solid was washed with deionized water, filtered off, and then dried at 373 K overnight. The dried zeolite sample was calcined for 6 h under atmospheric air at 773 K to eliminate the organic compound.

2.4 Ion exchange

For acid-base characters range of Na-mordenite, we did a post-synthesis cation exchange with Cs^+ and K^+ using the following process: In two different beakers, we introduce in the first one 100 ml of CsCl solution at 0.5 mol/l, and 100 ml of KCl solution at 0.5 mol/l in the second one. For each beaker 0.5 g of Na-mordenite zeolite was then added. Mixtures were stirred overnight in room temperature at low speed. After stirring operation had been completed, samples were filtered and washed with demineralized water three times at room temperature. Finally, they were dried overnight at 373 K and calcined under atmospheric air at 773 K for 6 h.

2.5 CO_2 adsorption

The carbon dioxide adsorption performance of the various exchanged mordenite samples was evaluated in the pressure range of 5 to 730 mmHg at 273 K, using CO_2 gas with high purity (99.999 %). The number of data points was 40. The adsorption measurement was carried out on Micromeritics ASAP 2020 apparatus. After each measurement, the adsorbed CO_2 molecules were desorbed by degassing gradually at 623 K for 4 hours to reach a vacuum.

3 Results and discussion

3.1 XRD

X-ray diffraction (XRD) pattern of the synthesized Na-Mordenite zeolite is illustrated on Fig. 1. The reflection peaks are represented between 2θ = 3° and 45°. The Fig.1. shows the presence of MOR structure peaks in the sample pattern and this is confirmed by characteristic peaks around 2θ ° (hkl) = 6.51 (110), 9.77 (200), 13.45 (111), 13.83 (130), 22.2 (150), 25.63 (202), 26.25 (350) [29].

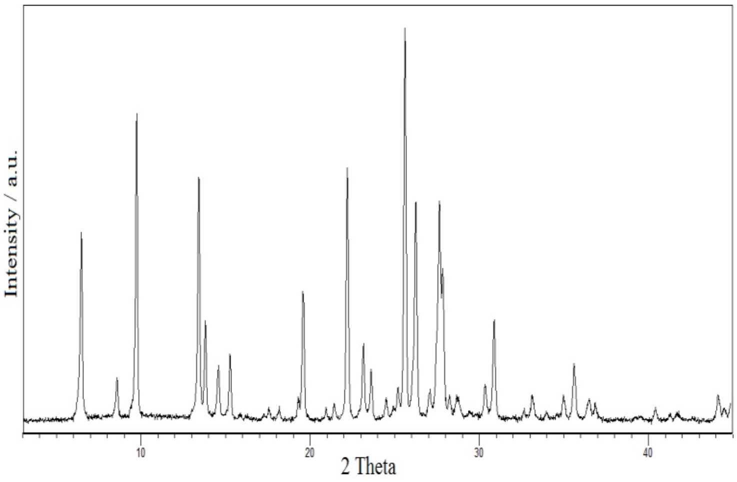

Fig.1. XRD pattern of synthesized Na-Mordenite.

3.2 SEM

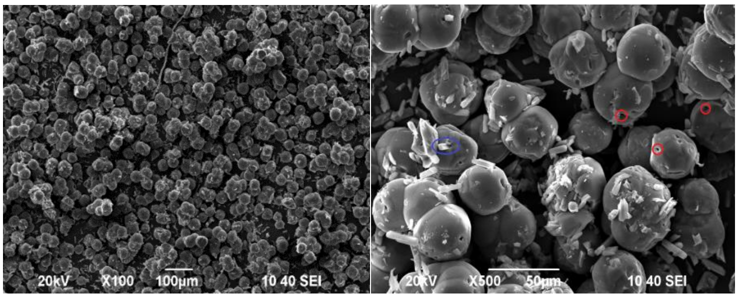

Fig.2. SEM images of non-calcined Na-Mordenite.

Fig.2. shows the SEM images of the synthesized Na-Mordenite. The images show large and uniform crystals with spherical shape and average diameter of 40 µm. The crystals contain large pores shown by the red circles due to the assembly of structural units around the condensed organic template in the synthesis gel (blue circles).

3.3 BET

Nitrogen adsorption-desorption isotherm at 77 K of calcined Na-Mordenite is presented in Fig.3. (a). The sample exhibits type IV isotherm which is a characterized by a level of saturation. This adsorption isotherm is obtained with mesoporous adsorbents in which occurs a capillary condensation. The saturation level indicates that, despite the increase in equilibrium pressure, there is no adsorption: this is interpreted by the fact that the mesopores, wherein occurred capillary condensation, are longer available for adsorption. The specific surface area is 319 m^2 g^{-1}. The hysteresis loop form is purely type H_1 that appears between relative pressure points 0.3 and 0.97. This type of hysteresis loop is often observed in the case of adsorbents having a very narrow pore distribution. The pore size distribution curve of the calcined sample is obtained using the Barrett–Joyner–Halenda (BJH) model. It is represented in the Fig.3. (b). Correspondingly to this figure, the average pore size distribution shows mesopores at 51 and 57 Å.

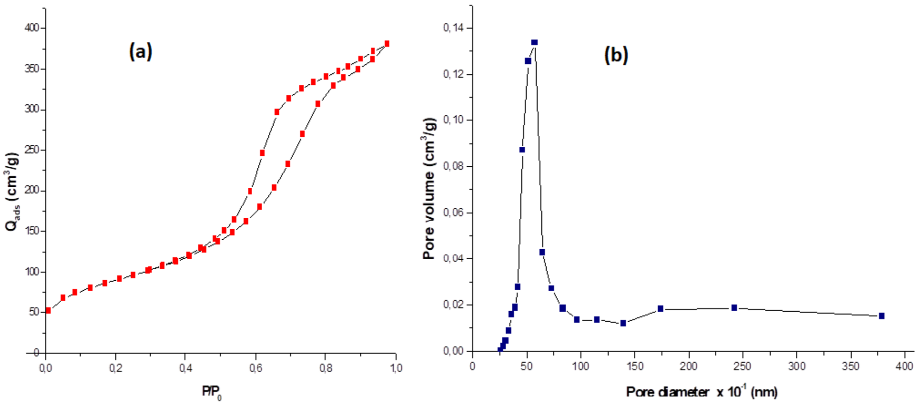

Fig.3. (a) N_2 adsorption-desorption isotherm of synthetized Na-mordenite (b) BJH pore size distribution of synthetized Na-mordenite.

3.4 CO_2 adsorption

In CO_2 adsorption by mesoporous mordenite part, we have introduced an alkalinity to this adsorbent by a post-synthesis treatment. Two alkaline cations (Cs^+ and K^+) were introduced by cation exchange with the sodium framework charge compensating of the zeolite to have three types of materials: Na-mordenite, K-mordenite, and Cs-mordenite. These adsorbents were then characterized by nitrogen adsorption-desorption manometry. The nitrogen adsorption-desorption isotherms at 77 K of the three adsorbents Na-mordenite, K-mordenite and Cs-mordenite are shown in Fig.4.

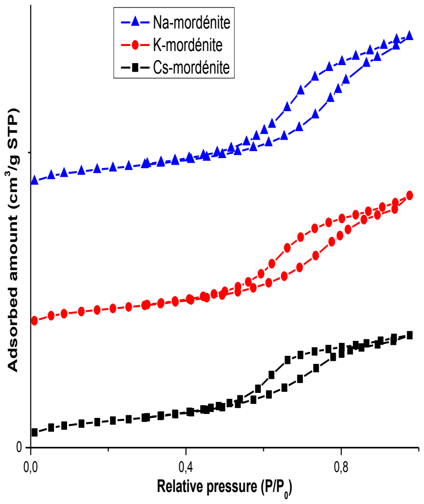

Fig.4. Nitrogen adsorption-desorption isotherms of the three adsorbents.

According to Fig.4., the three samples have Type IV isotherms characterized by a saturation level. This type of isotherm is obtained with mesoporous adsorbents in which capillary condensation occurs. It is clear according to the isotherms that the samples exhibit a mesoporous texture. The textural properties of the three samples are given in Table 1. According to the Table 1, we can remark the presence of a slight decrease in the pore volumes and the specific surfaces of K-mordenite and Cs-mordenite comparing to Na-mordenite. This can be explained by the existence of the two alkali cations K^+ and Cs^+, in the pores of the zeolites, which have a large atomic radius relative to the cation Na^+.

Table 1. Textural properties of different adsorbents.

Zeolite	Alkaline cation atomic radius (nm)	S_{BET} (m^2/g)	Pore diameter (Å)	Pore volume (cm^3/g)
Na-MOR	0.095	319	57	0.444
K-MOR	0.133	288	52	0.408
Cs-MOR	0.169	281	50	0.391

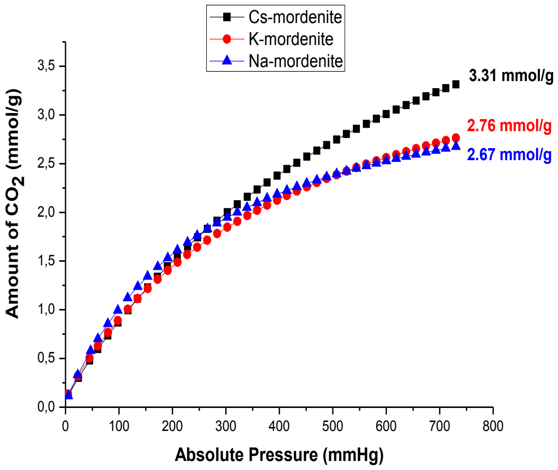

Fig.5. Carbon dioxide adsorption at 273 K by different mordenite.

Fig.5. shows the CO_2 adsorption isotherms by the different alkali-mordenite zeolites at 273 K. As mentioned on Fig.5., the CO_2 adsorption shows a regular variation of adsorbed amounts until upper pressure limit (730 mmHg) with optimal adsorption capacities of 2.67 mmol/g for Na-mordenite, 2.76 mmol/g for K-mordenite and 3.31 mmol/g for Cs-mordenite. The interesting adsorption rate of carbon dioxide in various zeolites was affected by the diffusion in micropores and mesopores formed in the mordenite structure. Since the sizes of the mesopores are much greater than that of the micropores, the mesopores volume and diffusion is generally much greater than the micropores and hence, zeolitic structures having mesopores exhibit higher capacity of adsorption notably at high pressure [30]. The other reason of increasing in capacities of CO_2 adsorption is the alkali cations [31]. The Fig.5. shows that adsorption is a function of alkali cations, since; adsorption capacities increases when cations basicity increases (from Sodium to Cesium). It is important to mention that similar behavior of increasing in CO_2 adsorption with increasing basicity of alkali metals has been observed in literature [32]. The alkali cations attribute an important forcefield between the CO_2 molecules and zeolite surface proven by Maurin *et al*. [33] in which the interaction parameters can be deduced from the polarizability of cations and adsorbate molecules.

4 Conclusion

Na-mordenite zeolite with expanded pores was synthesized using *N*,*N*-dimethylaniline as structure directing-agent. Ionic exchange treatment by Cesium and Potassium cations was performed to have various basic zeolites. The created mesopores into mordenite crystals and alkali cations are two factors that have assigned in the high adsorption capacity of molecules of carbon dioxide. Expanded pores attributed in fast intracrystalline diffusion, and alkali cations gave a significant basicity to capture CO_2 as an acid gas. According to the alkalinity and the atomic radius (Na<K<Cs), the CO_2 capture capacity was increased.

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